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(21) International Application Number: PCT/US00/12057 (22) International Filing Date: 2 May 2000 (02.05.00) (30) Priority Data: 09/304,486 3 May 1999 (03.05.99) US (71) Applicant: PQ HOLDING, INC. [US/US]; 103 Springer Building, 3411 Silverside Road, Wilmington, DE 19803 (US). (72) Inventors: BENNETT, Audrey, J.; 146 Josephine Avenue, West Conshohocken, PA 19428 (US). BERG, Kenneth, A.; 150 Mendham Drive, North Wales, PA 19454 (US). BROZZETTI, Adam, J.; 285 MacKensie Drive, West Chester, PA 19380 (US). (74) Agents: LEWIS, Christopher, R. et al.; Ratner & Prestia, 301 One Westlakes (Berwyn), P.O. Box 980, Valley Forge, PA 19482-0980 (US).		(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: PROCESS AND COMPOSITION FOR REDUCING CHILL HAZE IN BEVERAGES (57) Abstract <p>A process and composition for removing certain undesirable components from beverages which tend to form a haze upon chilling utilizes an adsorbent including a silica component and a tannic acid component. The form of the silica component includes a silica gel and a metal-substituted silica gel, preferably a magnesium-substituted silica xerogel. The form of the tannic acid component includes tannic acid powder, in which case the adsorbent is simply a physical blend of tannic acid powder and the silica component. The form of the tannic acid component also includes a reaction product of tannic acid formed on the silica component during formation, such as by washing the silica hydrogel with a tannic acid solution. The adsorbent is particularly well-suited to reducing chill haze in beer. In addition to removing proteins which cause chill haze, the adsorbent of the present invention tends to remove some other components such as iron, without requiring the time-consuming process steps of allowing adsorbent to settle and decanting the beverage as is normally the case with tannin chillproofing and without requiring excessive energy to be applied during filtration.</p>		

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PROCESS AND COMPOSITION FOR REDUCING CHILL HAZE IN BEVERAGES

FIELD OF THE INVENTION

5 The present invention pertains to removing certain proteins that lead to chill haze in beverages, such as beer, and to reducing iron levels in beverages.

BACKGROUND OF THE INVENTION

10 Beer and other beverages brewed from grains are complex solutions containing numerous organic solutes. Some of these compounds undergo reactions depending on how and how long the beverage is stored. One troubling reaction is the development of haze on aging and chilling. This haze is objectionable to consumers of the beverage.

15 As used herein, the term "beverage" shall mean any beverage which is susceptible to formation of haze upon chilling (i.e., "chill haze"). Such beverages contain naturally occurring proteins and other components, such as polyphenols, that form chill haze. Such beverages include beer, wine, and certain fruit juices. The term "beer" as used in the specification and claims includes many types of brewed beer, including lager, Pilsner, Munich beers and ale, porter, and stout.

20 A number of methods and products have been developed to remove the proteins which lead to chill haze. These methods or products are used before bottling and include the use of various adsorbents such as silica hydrogels and/or xerogels; calcium, aluminum, and magnesium silicates; several types of clays or minerals; and mixtures thereof.

25 When selecting an adsorbent to remove proteins which cause chill haze in beers, it is important to select an adsorbent which is selective to such proteins. For example, there are other proteins in beers which are desirably left in the beer through consumption. These proteins include foam-stabilizing proteins as well as other proteins that contribute to the body of the beverage.

Both silica gels and tannic acid have been used independently (e.g., added in sequential process steps or added separately) in the brewing process to adsorb and

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precipitate, respectively, the protein component of chill haze precursor in order to prolong colloidal stability in beer. Tannic acid is a soluble additive which is added to beer at the end of fermentation where it complexes with proteins and precipitates. It has been used alone and in combination with proteolytic enzymes for beer stabilization. It is also known to use tannic acid to reduce the iron content in beer. It is separated from the beer by allowing the precipitate to settle and decant the beer off of the top, followed by a final filtration.

Silica gels are insoluble processing aids added either into bulk treatment tanks or at a filter. They stabilize beer by adsorbing particular proteins that are generally responsible for haze formation. Silica gels have been used alone and in combination with other beer stabilizers, such as PVPP and isinglass. Due to their insoluble nature, silica gels can be readily removed from beer by filtration alone.

It is desirable to use a single adsorbent for beverages, especially beer, which removes proteins which form chill haze, reduces iron content, yet can be easily filtered, thereby avoiding the traditional methods of settling, decanting, then filtering. These traditional methods of settling, decanting, and filtering are time consuming and lead to decreased productivity and increased waste disposal costs.

SUMMARY OF THE INVENTION

In view of its purposes, the present invention provides a process and composition for removing certain natural, undesirable components from beverages. The process of the present invention involves contacting a beverage with an adsorbent comprising a silica component and a tannic acid component to adsorb at least a portion of the undesirable components onto the adsorbent thereby leaving a component-depleted beverage. After allowing a time sufficient for adsorption, the adsorbent is separated from the component-depleted beverage.

The composition of the present invention is an adsorbent comprising a silica component and a tannic acid component. The silica component may be either a silica gel, a metal-substituted silica gel, or a combination of both. In one embodiment of the present invention, the tannic acid component is tannic acid powder, and the adsorbent is formed by simply blending the tannic acid powder with a dried silica gel powder.

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According to another embodiment, the tannic acid component is a reaction product of tannic acid formed on the silica component in the manufacture of the adsorbent.

The process and composition of the present invention provide for the removal of certain trace components from beverages. These components include iron and proteins which form haze upon chilling. The process and composition of the present invention allow for the removal of such components without requiring the time-consuming process steps of allowing an adsorbent to settle and then decanting the beverage and without requiring an excessive amount of energy to be applied during filtration.

The present invention is also directed to methods for making the adsorbents of the present invention.

It is to be understood that both the foregoing general description and the following detailed description are exemplary, but not restrictive, of the invention.

BRIEF DESCRIPTION OF THE DRAWING

The invention is best understood from the following detailed description when read in connection with the accompanying drawing, in which:

FIG. 1 is a schematic view of an embodiment of a process for making an adsorbent according to the present invention;

FIG. 2 is a graphical representation of the ppb iron contributed to beer by a tannic acid/silica gel blend at varying amounts of tannic acid, in weight percent;

FIG. 3 is graphical representation of the ppb iron contributed to beer at various contact times of three different adsorbents with the beer; and

FIG. 4 is a graphical representation of the weight percent of bound and total sodium and magnesium in various samples of an adsorbent prepared by the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a process and composition for removing certain undesirable components of beverages to produce beverages with substantially lowered concentrations of these trace components. As used herein, the term

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"beverages" is intended to encompass all beverages which include certain proteins which, if left in the beverage, tend to form haze upon chilling but can be adsorbed by the present invention. Such beverages include wine, fruit juices, and beer, to which the present invention is particularly applicable.

5 The proteins which cause haze are generally characterized as containing bound polyphenol. Other proteins, on the other hand, may have carbohydrates bound to them and include certain desirable proteins, such as those which stabilize foam in beer. The adsorbent of the present invention selectively adsorbs haze-forming proteins without adsorbing foam-stabilizing proteins.

10 As used herein, the term "removing" as in "removing components from beverages" implies removing at least some percentage of selected components, such as the proteins which cause chill haze and iron (which adversely affects colloidal and flavor stability), but does not necessarily contemplate removing one hundred percent of any of these components. In some cases, however, a component may be removed to such an
15 extent that it cannot be detected by known quantitative analysis procedures. The adsorbent of the present invention might remove some portion of other components, such as copper, but no component or contaminant other than iron has been tested.

 In its most general form, the adsorbent of the present invention is an adsorbent comprising a silica component and a tannic acid component. Methods of
20 making the adsorbent of the present invention are discussed in connection with the accompanying FIG. 1, in which the silica component is a metal-substituted silica xerogel.

 The first step of a method for making an adsorbent of the present invention, in which the silica component is a metal-substituted silica xerogel, is the partial neutralization of a sodium silicate or a potassium silicate solution to form a silica
25 hydrosol. In particular, silica hydrosols are formed by rapidly mixing aqueous solutions of an acid and sodium or potassium silicate. For example, an acid source 10 may be used to supply an acid, such as sulfuric acid, which is combined with the sodium or potassium silicate solution from silicate solution source 12. The concentrations and flow rates or proportions are adjusted so that the hydrosol contains 8 to 12% SiO₂ and so that only sixty
30 to ninety-nine percent of the alkali metal present in the silicate solution is neutralized and,

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most preferably, seventy to ninety-five percent of the alkali metal is neutralized. Thus, a portion of the alkali metal remains with the silica hydrosol, represented as unreacted Na_2O or K_2O .

The silicate/acid mixture is forced through a nozzle 14. From the nozzle, the hydrosol mixture forms hydrogel beads 16, which are allowed to set to form a hydrogel, all in a known manner. Such hydrosol mixtures gel rapidly and can be allowed to gel in a mass and then be crushed (or granulated) to form discrete hydrogel particles for further processing. In one embodiment the hydrosol contains about 10% SiO_2 , has a pH above about 8, and gels in a matter of seconds or less. Such a hydrosol can be formed into spheres by spraying in air.

According to the embodiment shown, the hydrogel is then delivered to a bath of a solution of a multivalent metal in exchanger 18. Multivalent metals used to prepare compositions of the present invention are those having ions which can react with the unreacted sodium or potassium ions on the silica surface and within the silica particles in a reversible manner. In other words, the metal ions must be capable of adsorbing or desorbing from silica in response to changes in pH and/or concentration. The metal ions selected also have a greater affinity of adsorption of at least some of the trace components than sodium or potassium, whose ions are replaced by ions of the substituting metal. Preferably, the metal ions of the substituting material have a strong affinity for adsorbing the components which are sought to be removed. Also, the metals should preferably not be metals which have been found to be detrimental to the taste, color, stability, or odor of the beverage, such as iron, copper, or phosphorous. Among useful metals are magnesium, aluminum, calcium, barium, manganese, and mixtures thereof, with magnesium and calcium being more preferable and magnesium being the most preferable.

The substituting metal can exist in solution as the ionized form of a metal salt, with a halide, phosphate, nitrate, sulfate, acetate, or oxylate as counter ions to the metal ions in the solution. Preferably, the metal salt is magnesium sulfate. The concentration of the metal ion in the solution should be sufficient to promote reaction (i.e., substitution of the alkali metal ions) of the metal with the silica but not favor precipitation or aggregation of metal species. Typically, the concentration of the metal

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ions to achieve this function is between about 0.3% to 10% by weight, and preferably between about 3% to 7% by weight.

In exchanger 18, the hydrogel particles are contacted with an aqueous solution of a metal salt, such as magnesium sulfate, for a period of time sufficient to replace essentially all of the unreacted sodium or potassium on the surface of, and within, the silica particles with the substituting metal. Contact times depend on the particular conditions and typically vary between fifteen minutes to six hours. The metal-depleted and sodium- or potassium-enriched effluent is withdrawn from exchanger 18 in stream 20. The metal ion bath may be replenished and buffered as needed by metal ion bath feed tank 22. Because the metal in the metal ion solution, such as magnesium, has now replaced most of the sodium or potassium ions within the silica gel, the hydrogel can now be characterized as "metal-substituted silica hydrogel."

FIG. 4 shows the extent to which magnesium replaces sodium in a metal-substituted silica xerogel in the present invention. In particular, numerous samples of a metal-substituted silica xerogel were prepared according to the process set forth in Example 1 below. The wet weight percentages of total and unbound sodium and magnesium in the final product (i.e., the xerogel) were then tested and are shown in Fig. 4 for nineteen samples. As shown in FIG. 4, the weight percent of bound magnesium varies between about 1.0% and 1.3%, while the weight percent of bound sodium is about 0.1% or less. Thus, about 90% or more of the previously bound sodium (i.e., the sodium which was integral to the silica gel structure) is replaced by magnesium. The unbound sodium and magnesium is merely a measure of the extent of water washing, as discussed in Example 1 and in the paragraph below. These unbound ions exist as water soluble salts.

The metal-substituted silica hydrogel is next delivered to a wash extractor 24 via stream 26. In an embodiment in which the tannic acid component is not added until later, wash extractor 24 contains only deionized water to remove salts and any excess acid. Multiple washings may occur with the effluent being withdrawn in line 30 and the washed, metal-substituted silica hydrogel being delivered to a milling/drying unit 32 via line 34.

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On the other hand, in an embodiment in which the tannic acid component is added during this wash step, the solution used to wash the metal-substituted silica hydrogel is an aqueous tannic acid solution. In this embodiment, the function of the wash solution is not only to remove salts and any excess acid but also to cause a reaction
5 between the tannic acid and the metal-substituted silica hydrogel.

In milling/drying unit 32, the hydrogel (or the adsorbent including the silica and tannic acid components) is dried. The gels can be dried to anywhere from between about 0.01 % to 25% moisture content, preferably between about 8% and about 15%, and most preferably about 10% to form a metal-substituted silica xerogel of the
10 present invention. Milling continues until the average particle size is between about 10 to about 40 microns, although the particular size will depend on the needs of the end use and other conditions in the beverage purification process. In general, the particles should be in the form of a powder and should not be milled too small such that filtration becomes difficult.

In the event that the tannic acid component was added during the wash
15 extractor step, the adsorbent of the present invention can then be delivered via line 36 to packaging unit 38, where the product is packaged. Alternatively, or in addition to adding the tannic acid component via the wash extractor step, tannic acid powder can be blended with the dried powder from milling/drying unit 32 prior to packaging. In this
20 embodiment, tannic acid source 40 is used to deliver tannic acid powder to line 36 where the tannic acid intermixes with the dried powder (i.e., either the silica component or, in the case where tannic acid has been previously added, the adsorbent including both the silica component and the tannic acid component). As used herein, the term "blending" means that the tannic acid powder is physically mixed with (but not chemically reacted
25 with), the powder from the milling/drying unit. The resultant blend is thus merely a physical mixture of two powders, which are chemically inert relative to one another.

The tannic acid powder may be certain commercially available tannic acid powders. An exemplary tannic acid is a tannic acid anhydride (USP grade) sold by Fuji. Regardless of where the tannic acid is added, the particular tannic acid used can be any
30 known tannic acid which shows some reduction in iron content or proteins which form

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chill haze in beverages treated by an adsorbent of the present invention. Although all tannic acids tested achieved these functions to some degree, it is preferable that the tannic acid used is hydrolyzable tannic acid, as opposed to derivatives of flavanols (i.e., condensed tannins). Hydrolyzable tannic acids are esters of a sugar, usually glucose, with one or more trihydroxybenzenecarboxylic acid. More preferably, the tannic acid used is produced from Chinese nutgall.

The tannic acid may be added at other points during the production of the adsorbent of the present invention, although it has not been confirmed that the addition of tannin achieves the purposes of the present invention at any other points than the two discussed above. Nonetheless, adding the tannic acid to the magnesium exchange bath might result in an adsorbent which reduces iron content and proteins which form chill haze. In addition, the tannic acid might also be added as the adsorbent enters the milling/drying unit, although the form of the adsorbent is a wet bulky material which might not be too accommodating. As shown by the examples below, the preferred embodiment is blending the tannic acid powder with the silica component in powder form. This embodiment appears to achieve the best results, with respect to the removal of iron and proteins which form chill haze and in minimizing the force required to filter the adsorbent from the beverage.

The concentration of tannic acid can vary over a wide range depending on the same factors discussed above. The tannic acid appears to be particularly suitable in adsorbing iron. Accordingly, when the beverage contains a large concentration of iron, then a commensurately larger percentage of tannic acid should be used. It has been found that, for some of the beverages tested, tannic acid can be added to achieve a concentration of about 0.1% to about 10% tannic acid of the adsorbent, on a dry weight basis.

Preferably, the concentration of tannic acid is about 0.5% to about 2.0% tannic acid of the adsorbent. In the embodiment where the tannic acid component is added during the wash step, the concentration of tannic acid may vary over a wide range and may preferably be between 0.01% (by volume) to 3.0%, and more preferably 2.0% to 2.5%.

Another embodiment of the process to prepare the product of the present invention involves the preparation of a silica gel wherein the hydrosol has an acidic pH

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value. According to this embodiment, more than sufficient acid is added to neutralize all of the sodium initially present in the silicate. The resulting gel is washed to remove salts and excess acid. Then, an alkaline solution such as NaOH or KOH is added to the silica gel slurry to provide a pH above about 8, preferably between about 8.3 and about 9, for a time sufficient to allow at least some of the sodium or potassium to become associated with the silica gel. This alkalized or alkaline gel is contacted with a solution of a metal salt, such as magnesium sulfate, for a time sufficient to exchange the sodium or potassium ions associated with the silica gel with magnesium ions.

The pH of the adsorbent of the present invention is at least about 6, and typically at most about 9, and preferably between about 7 and about 8.5, and most preferably about 8.2. The pH of the metal ion solution (also described as the "alkaline solution") must be controlled and may be adjusted during the reaction of the substituting metal with the silica. The agent used to adjust the pH may be any known agent that can achieve and maintain the required pH value in solution while the solution is exposed to silica. Acids, bases, and various buffers can be used as this adjusting agent in a known manner. For most metals, the pH of the alkaline solution should be maintained at a value of between about 7 and about 10.5, and preferably between about 8 to 9.5. Acidic pH values during the substitution of the metal ions tend to cause precipitation of metal oxides in and around the silica particles. Such precipitates tend to be relatively large and tend to block the pores of the silica, thereby reducing efficiency of adsorption.

In the embodiment in which the silica component is a metal-substituted silica gel, the metal is usually a metal with a valence of two or more. Typical ranges of the constituents of the silica component are shown below in Table 1:

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Table 1

	% by Weight (Wet)
Metal	0.5 – 15.0
SiO ₂	99.34 – 94.0
H ₂ O	0.01 – 25.0

More preferably, metal is added to 0.5 to 3.5% (wet weight). The most preferred substituting metal ion is magnesium, and preferably 0.5 to 5% (wet weight) of the xerogel is present as magnesium.

5 According to the embodiment in which the silica component is merely a silica gel, the same general process is used, except that the ratio of acid to silicate solution is selected such that all of the sodium or potassium is neutralized and there is no metal exchange step in this process. In particular, according to this process, the fully acid
10 neutralized silica hydrosol is ejected through nozzle 14 and forms hydrogel beads 16, which are then delivered directly to wash extractor 18, which may or may not contain tannic acid, depending on the manner in which tannic acid is to be added.

 Regardless of the specific type of silica component used, it is important to use a silica component having a pore diameter which serves to adsorb a relatively high
15 percentage of haze-forming proteins without adsorbing too many foam-stabilizing proteins. It has been found that a silica component having an average pore diameter of between about 50 to about 150 Angstroms is desirable for most applications, although this could change depending on the nature of the beer.

 Achieving such a pore diameter is well-known in the art. For example, exposing the silica gel to elevated temperatures at alkaline pH leads to a rearrangement of
20 the gel structure; surface area is reduced and the mean pore diameter of the final product is increased. This process is known in the art as "hydrothermal treatment." An acid-set gel needs to be adjusted to alkaline or neutral pH for this to occur, but an alkaline-set gel need only be held at an elevated temperature for some period of time. Drying conditions will also affect porosimetry properties; rapid drying tends to result in higher pore
25 volumes. The silica content of the hydrosol also affects porosimetry. All of these effects are well-known to those skilled in the art and are described in many publications and patents.

 The adsorption step is accomplished by simply contacting the adsorbent of the present invention with the beverage, preferably in a manner which facilitates the

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adsorption, in a conventional manner. The adsorption step may be any convenient batch or continuous process. In any case, agitation or other mixing will enhance the adsorption efficiency of the adsorbent.

Adsorption may be conducted at any convenient temperature at which the beverage is a liquid. Typically, the beverage temperature is between about 29° and 40°F. The beverage and adsorbent are contacted as described above for a period of time sufficient to achieve the desired component percentage reduction in the treated beverage. The specific contact time will vary somewhat on the selected process, i.e., batch or continuous; with the type and condition of the beverage to be treated; with the concentration of the components in the beverage; and with the particular adsorbent being used. In cases where the contact time is already set, the particle size of the adsorbent may be varied in a known way to meet the various process conditions. In addition, the relative quantity of adsorbent brought into contact with the beverage will also affect the amount of components removed. The amount of adsorbent added to the beer is measured in parts per million (e.g., grams of adsorbent per 1,000,000 gram of beer). The adsorbent usage may be from about 100 ppm to about 1,000 ppm, and preferably from about 400 ppm to about 800 ppm.

During the refinement of beer, other additives are sometimes used to adsorb components and to perform other functions. The adsorbent of the present invention achieves the functions of the present invention in the presence of other known additives in the industry. For example, foam stabilizers, anti-oxidants, perlite, and diatomaceous earth are often added to beer prior to filtering. Diatomaceous earth, for example, is used as a filter aid but often undesirably contributes iron to the beer. Some of the iron removed by the adsorbent of the present invention is iron contributed by the diatomaceous earth.

Regardless of the particular adsorbent of the present invention used, the adsorbent (or adsorbents) is separated from the component-depleted beverage in any known manner following adsorption. For example, a filtration device may be used to separate the adsorbent from the component-depleted beverage. The separation may be effected by one or more filtering stages.

EXAMPLES

The following examples are included to more clearly demonstrate the overall nature of the invention. These examples are exemplary, not restrictive, of the invention.

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A silica hydrosol containing 12% of SiO₂ was prepared by rapidly mixing solutions of sulfuric acid and sodium silicate. The acid solution had a concentration of 10.5% H₂SO₄ and a temperature of about 85°F. The silicate solution had a nominal SiO₂:Na₂O weight ratio of 3.2, a solids level of 30.5%, and a temperature of about 85°F. The flow rates of the acid and silicate solutions were adjusted such that 90% of the sodium in the silicate was neutralized; the pH was above about 8. The hydrosol was sprayed into the air and allowed to form into spheres. The gel time was less than one second.

The gelled spheres were introduced into an aqueous solution of magnesium sulfate. The sulfate solution contained about 14% MgSO₄ and had a temperature of about 160°F. Sufficient time was allowed for essentially all of the unneutralized sodium to exchange with magnesium. The magnesium substituted silica hydrogel was washed with water to achieve a concentration of less than 1% water-soluble salts by weight in the final xerogel product. The gel was dried to a loss-on-drying of about 12% and milled to a median particle size of about 14-15 micrometers. The final product contained about 1.2% magnesium, which is nearly stoichiometrically equivalent to the unneutralized sodium in the initially formed gel spheres.

The chillproofing experiments were carried out as follows. Untreated beer was refrigerated at 0°C during storage and handling, and protected against oxygen by CO₂. The headspace O₂ level was less than 100 ppb during all handling. Time contact with the chillproofing agent started when an aliquot of beer was transferred into a tank containing a stirred deoxygenated slurry of chillproofing agent and body feed. The slurry contained 10% (w/v) chillproofing agent, and the volume was varied to provide the dose of agent desired. After the required contact time, the beer slurry was pumped through a filter. After filtering, the beer was bottled anaerobically against CO₂ back pressure. The bottled beer was forced by incubation at 60°C for five days, then stored at 0°C for two days. Forcing, or force testing, is accelerated shelf life testing where beer is held at an elevated temperature for a period of days or weeks, which accelerates haze formation to simulate weeks or months of aging at ambient temperatures.

The haze was measured with an LG Automatic Haze Meter filled with ice water, and the units are ASBC FTU. The instrument is standardized each day using membrane filtered water and a 431 FTU standard.

Example 1

Table 2 shows the chill haze and filtration pressure required of three samples the same beer, which was a lager of about 70% malt, namely beer sold under the

registered trademark Budweiser, commercially available from Anheuser-Busch. The three different samples were: (i) not treated; (ii) treated by metal-substituted silica xerogel made as described above under "Examples"; (iii) treated by the metal-substituted silica xerogel then subsequently treated separately by tannic acid solution available from Fuji; and (iv) treated by the metal-substituted silica xerogel blended with the same tannic acid powder. The normal dose of tannic acid used in the beer in Table 1 is 16 gallons of 4% aqueous tannic acid solution per 350 barrels ("BBL") of beer. One-tenth of that dose was used here which is approximately equal to 1% tannic acid on a weight-weight basis.

Filtration ΔP (i.e., pressure differential) is the pressure across the filter after X BBL/ft.² Filtration ΔP was determined by in-line pressure sensors located before and after the filter membrane. The pressure reading after the filter is subtracted from the pressure reading before the filter for the ΔP . In the examples provided, the ΔP reported is the highest ΔP [in psi] achieved during the filtration.

It can be seen that when used together, the metal-substituted silica gel and tannic acid gave superior chillproofing performance without much increase in the pressure differential across the filter, when compared to the metal-substituted silica xerogel alone. Silica gel followed by a separate treatment of tannic acid also did not perform as well as the combination with regard to haze reduction, and filtration rates were unacceptable.

Table 2

Treatment	Dose (ppm)	Chill haze (ASBC FTU) Trial #1	Filtration ΔP (psi) Trial #1	Chill haze (ASBC FTU) Trial #2	Filtration ΔP (psi) Trial #2	Chill haze (ASBC FTU) Trial #3	Filtration ΔP (psi) Trial #3
No treatment	0	343	14	375	16	971	14.5
Silica gel	600	86	21	78	22	246	21.5
Silica gel followed by tannic acid	600 + 1/10 t.a..	113	30	92	36	553	36
Silica gel blended with tannic acid [powder]	600 + 1/10 t.a..	65	24	63	26	150	22.5

Example 2

Finished Budweiser, available from Anheuser-Busch, with an untreated iron level of 42 ppb, was treated with the metal-substituted silica xerogel blended with tannic acid powder referred to in the fourth row of Table 2 above. The adsorbent was filtered out of the beer and iron content was determined in the beer both untreated and after treatment with varying concentrations of tannic acid. The results are shown in Table 3 below.

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Table 3

% Tannic Acid	Ppb Fe
0	61
0.5	48
1.0	36
1.5	32
2.0	21
2.5	15

It should be noted that the untreated beer had an iron content of 42 ppb Fe. Thus, a tannic acid addition of between 0.5% to 1.0% first shows a decrease in the iron content over that which is inherent in the beer.

Example 3

A sample of Budweiser and of Stroh's Ballantine Ale were tested for chill proofing performance, as described above. The same metal-substituted silica xerogel used in the previous examples was used, with varying amounts of tannic acid added, shown in weight percent. The results are shown in Table 4.

Table 4

% Tannic Acid	Budweiser (ASBC FTU)	Ballantine Ale (ASBC FTU)
Untreated	1091	343
0	170	163
0.5	193	152
1.0	180	133
1.5	138	138
2.0	125	130
2.5	153	159

In Stroh's Ballantine Ale, performance began to improve with the lowest level of tannin addition (0.5%). Addition of 1% tannin in the blend gave an additional boost of performance and no further improvement was seen as more tannin was added to the blend. Performance began to drop off when the tannin level in the blend reached 2.5%.

This drop may be due to an excess of tannin over the amount of protein present.

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In centrifuged Budweiser beer, the optimum level of tannin in the blend seemed to be different from that for Ballantine Ale. In Budweiser beer, 0.5% tannin in the blend actually chillproofed slightly worse than the control (0%), and the blend containing 1% tannin was no better (within experimental error) than the control. Performance was improved with the blends containing 1.5% and 2.0% tannin, but the same drop-off in performance was seen when 2.5% tannin was incorporated in the blend. The chillproofing for this study was done using a 30 minute contact time.

Example 4

A tannic acid washed metal-substituted silica xerogel was formed by using a tannic acid solution in the wash extractor step as opposed to simply deionized water. Various tannic acid solutions of increasing strength were used to achieve an adsorbent having 0.5% (weight percent) tannic acid, 1.0% tannic acid, and 2.0% tannic acid, respectively. Other than this addition of tannic acid, the magnesium-substituted silica xerogel was made as described above. The beer used was Budweiser. It was tested for iron content after being treated with the magnesium-substituted silica xerogel alone as well as with the three tannic acid washed adsorbents. The results are shown below in Table 5.

Table 5

% Tannic Acid	Ppb Fe
0	74
0.5	31
1.0	21
2.0	25

It should be noted that, for the tannic doses referred to above, 0.018 grams of tannin per gram wash water were added for a 1% dose, 0.009 grams of tannic acid per gram of wash water was added for a 0.5% tannin dose, and 0.0036 grams of tannic acid per gram of wash water was added for a 2% tannin dose. In this case, the hydrogel had approximately 18% solids. In preparation of these tannic acid washed gels, 100 grams of hydrogel were added to one hundred milliliters of solution and held at 71.1°C for twenty-four hours. The hydrogel beads were drained of wash solution dried over a two day period at 120°C.

A sample of the same blends were then tested for chillproofing performance of Budweiser beer, as described above. The results are shown in Table 6.

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Table 6

% Tannic Acid	Budweiser (ASBC FTU)
Untreated	1091
0	115
0.5	212
1.0	131
2.0	117

As shown from Table 5, the 0.5% tannic acid-washed gel performed significantly worse than the water-washed control silica gel. As more tannin is incorporated into the gel, performance begins to improve. Even at tannin loading of 2%, however, it is only improved to the point of being equal to the control with no tannin added. Another test with a beer having an untreated force total haze value of 195 ASBC FTU and a value of 74 ASBC FTU for the water wash control, showed values of 70 and 68 ASBC FTU at 2% tannic acid wash gel in two different batches, thus showing some slight improvement over the control. Further tests were conducted to determine the total magnesium content which was removed from the gel by the tannic acid washing. It appears that over half of the magnesium is removed even with an addition as low as 0.5% tannic acid, which might cause the reduced performance in chill haze results.

Example 5

Blends of tannic acid to varying percentages with the silica gel made as described above containing 1.2% magnesium were used in forcing tests a five days at 60°C then two days at 0°C. The results of the standard chillproofing tests for Colt 45 Malt Liquor, Budweiser, and Bud Light are shown below in Table 7. In this example, the tannic acid was merely blended with the silica gel.

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Table 7

% Tannic Acid	Colt 45 (ASBC FTU)	Budweiser (ASBC FTU)	Bud Light (ASBC FTU)
Untreated	365	638	970
0	219	117	--
0.5	201	--	--
1.0	194	--	--
1.5	199	98	290
2.0	172	--	--
2.5	186	--	--

Table 7 shows that the 1.5% tannic acid resulted in a 10-20% improvement in forced total haze in each of these experiments. As can be seen for the number of tests for Colt 45, any tannic acid addition in that case showed some reduction in haze formation.

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Example 6

Low levels of tannic acid were added (as a blend) to the silica gel described above to determine what level is needed to achieve zero iron contributed to beer (with no extra iron removal). More specifically, it has been determined that the silica gel described above undesirably contributes some iron to the beer, while the tannic acid removes some of the iron. The results are shown in FIG. 2 along with results from earlier experiments at higher levels of tannin addition. Zero added iron is seen somewhere between 0.5 and 0.75% tannin added.

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FIG. 3 shows the iron contributed the beer at various contact times for untreated beer, the silica gel with no tannic acid as described above, and a 1.5% tannic acid/silica gel blend as described above. Iron content was measured at 10 minutes and 24 hours. As can be seen, there is very little change in the amount of iron removed from ten minutes to twenty-four hours of contact with the blend, while about 60% of the iron from the silica gel to beer is released within ten minutes.

15

Example 7

Tests were also conducted to show the effects of diatomaceous earth (DE) addition on iron content in beer treated with the 1.5% tannic acid/silica gel blend described above. As discussed above, diatomaceous earth is a large contributor of beer-soluble iron. The two grades of diatomaceous earth used are Celite 512 and Celite 3Z (which is premium low-iron grade) and they contribute 33 and 16 ppb iron, respectively. A ten minute diatomaceous earth contact time was chosen for these experiments because diatomaceous

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earth is injected into the beer in line on the way to the filter, so it has a very short contact time. In each case, the loading of DE was 800 ppm. The results are shown below in Table 8.

Table 8

Adsorbent	ppb Iron Contributed to Beer
1.5% tannin/silica gel blend	-17
512 diatomaceous earth	33
3Z diatomaceous earth	16
1.5% tannic acid/silica gel blend plus 512 DE @ 24 hr.	-5
1.5% tannic acid/silica gel blend plus 3Z DE @ 24 hr.	0
1.5% tannic acid/silica gel blend plus 512 DE @ 10 min.	18
1.5% tannic acid/silica gel blend plus 3Z DE @ 10 min.	8

As can be shown from the Table 8, if DE is added to beer treated with a tannin/silica gel blend with a contact time of 10 minutes, there is about a 50% reduction amount of iron contributed by the DE. If the DE were allowed to contact the tannin-treated blend for 24 hours, there would be no iron contributed to beer from the DE or from the chillproofer.

Although illustrated and described herein with reference to certain specific embodiments and examples, the present invention is nevertheless not intended to be limited to the details shown. Rather, various modifications may be made in the details within the scope and range of equivalents of the claims and without departing from the spirit of the invention.

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What is Claimed:

1. A process for removing components from a beverage to reduce chill haze, said process comprising the steps of:

5 contacting a beverage with an adsorbent comprising a silica component and a tannic acid component to adsorb at least a portion of said components onto said adsorbent thereby leaving a component-depleted beverage; and

 separating said adsorbent from said component-depleted beverage.

2. A process in accordance with claim 1, wherein:

10 said silica component is selected from the group consisting of at least one of a silica gel and a metal-substituted, silica gel;

 said tannic acid component comprises tannic acid powder; and

 said adsorbent comprises a blend of said silica component and said tannic acid powder.

3. A process in accordance with claim 1, wherein:

15 said silica component is selected from the group consisting of at least one of a silica gel and a metal-substituted, silica gel; and

 said tannic acid component comprises a reaction product of tannic acid formed on said silica component.

20 4. A process in accordance with claim 3, wherein said reaction product is formed during washing of a silica hydrogel with a tannic acid solution.

5. A process in accordance with claim 1, wherein said silica component is a magnesium-substituted silica xerogel.

25 6. A process in accordance with claim 5, wherein said magnesium-substituted silica xerogel is made by contacting a silica hydrogel with an alkaline solution containing said magnesium to form a magnesium-substituted silica hydrogel and then drying said magnesium-substituted silica hydrogel sufficiently to form said magnesium-substituted silica xerogel.

7. A process in accordance with claim 5, wherein said xerogel has a moisture content of between about 0.01% and about 25%.

30 8. A process in accordance with claim 1, wherein said adsorbent is added to said beverage in an amount to achieve a concentration of about 100 ppm to about 1,000 ppm and comprises about 0.1% to about 10% tannic acid, on a dry weight basis.

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9. A process in accordance with claim 8, wherein said adsorbent is added to said beverage in an amount to achieve a concentration of about 400 ppm to about 800 ppm and comprises about 0.5% to about 2.0% tannic acid, on a dry weight basis.

10. A process in accordance with claim 1, wherein the step of separating comprises filtering said adsorbent from said component-depleted beverage.

11. A composition for use in the removal of components from a beverage to reduce chill haze, said composition comprising an adsorbent comprising a silica component and a tannic acid component.

12. A composition in accordance with claim 11, wherein:
said silica component is selected from the group consisting of at least one of a silica gel and a metal-substituted, silica gel;
said tannic acid component comprises tannic acid powder; and
said adsorbent comprises a blend of said silica component and said tannic acid powder.

13. A composition in accordance with claim 11, wherein:
said silica component is selected from the group consisting of at least one of a silica gel and a metal-substituted, silica gel; and

said tannic acid component comprises a reaction product of tannic acid formed on said silica component.

14. A composition in accordance with claim 13, wherein said reaction product is formed during washing of a silica hydrogel with a tannic acid solution.

15. A composition in accordance with claim 11, wherein said silica component is a magnesium-substituted silica xerogel.

16. A composition in accordance with claim 15, wherein said magnesium-substituted silica xerogel is made by contacting a silica hydrogel with an alkaline solution containing said magnesium to form a magnesium-substituted silica hydrogel and then drying said magnesium-substituted silica hydrogel sufficiently to form said magnesium-substituted silica xerogel.

17. A composition in accordance with claim 15, wherein said xerogel has a moisture content of between about 0.01% and about 25%.

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18. A composition in accordance with claim 11, wherein said adsorbent is added to said beverage in an amount to achieve a concentration of about 100 ppm to about 1,000 ppm and comprises about 0.1% to about 10% tannic acid, on a dry weight basis.

5 19. A composition in accordance with claim 18, wherein said adsorbent is added to said beverage in an amount to achieve a concentration of about 400 ppm to about 800 ppm and comprises about 0.5% to about 2.0% tannic acid, on a dry weight basis.

20. A method for making an adsorbent for use in the removal of components from a beverage to reduce chill haze, said method comprising:

10 combining a sodium silicate solution or a potassium silicate solution with a solution of an acid to form a silica hydrosol;

allowing said hydrosol to set to a hydrogel;

granulating said hydrogel into discrete hydrogel particles;

15 washing said discrete hydrogel particles with an aqueous tannic acid solution for a time sufficient to allow tannic acid to form a reaction product on said discrete hydrogel particles to form a reacted silica material; and

drying and milling the reacted silica material to form said adsorbent.

21. A method in accordance with claim 20, wherein the combining step comprises selecting the compositions and proportions of said silicate solution and said acid solution such that 60% to 99% by weight of the sodium or potassium in the silicate solution is neutralized and said method further comprises, prior to the washing step, contacting said
20 discrete hydrogel particles with a solution of a salt of a multivalent metal and maintaining the pH of the mixture of the hydrogel and solution at a value between about 7 and 10.5, to allow said metal to exchange with the sodium or potassium to form a metal-substituted, silica hydrogel.

25 22. A method in accordance with claim 20, wherein the drying step continues until said reacted silica material has a moisture content of between about 0.01% and about 25%.

23. An adsorbent formed by the process of claim 20.

30 24. A method for making an adsorbent for use in the removal of components from a beverage to reduce chill haze, said method comprising:

combining sodium silicate solution or a potassium silicate solution with a solution of an acid to form a silica hydrosol;

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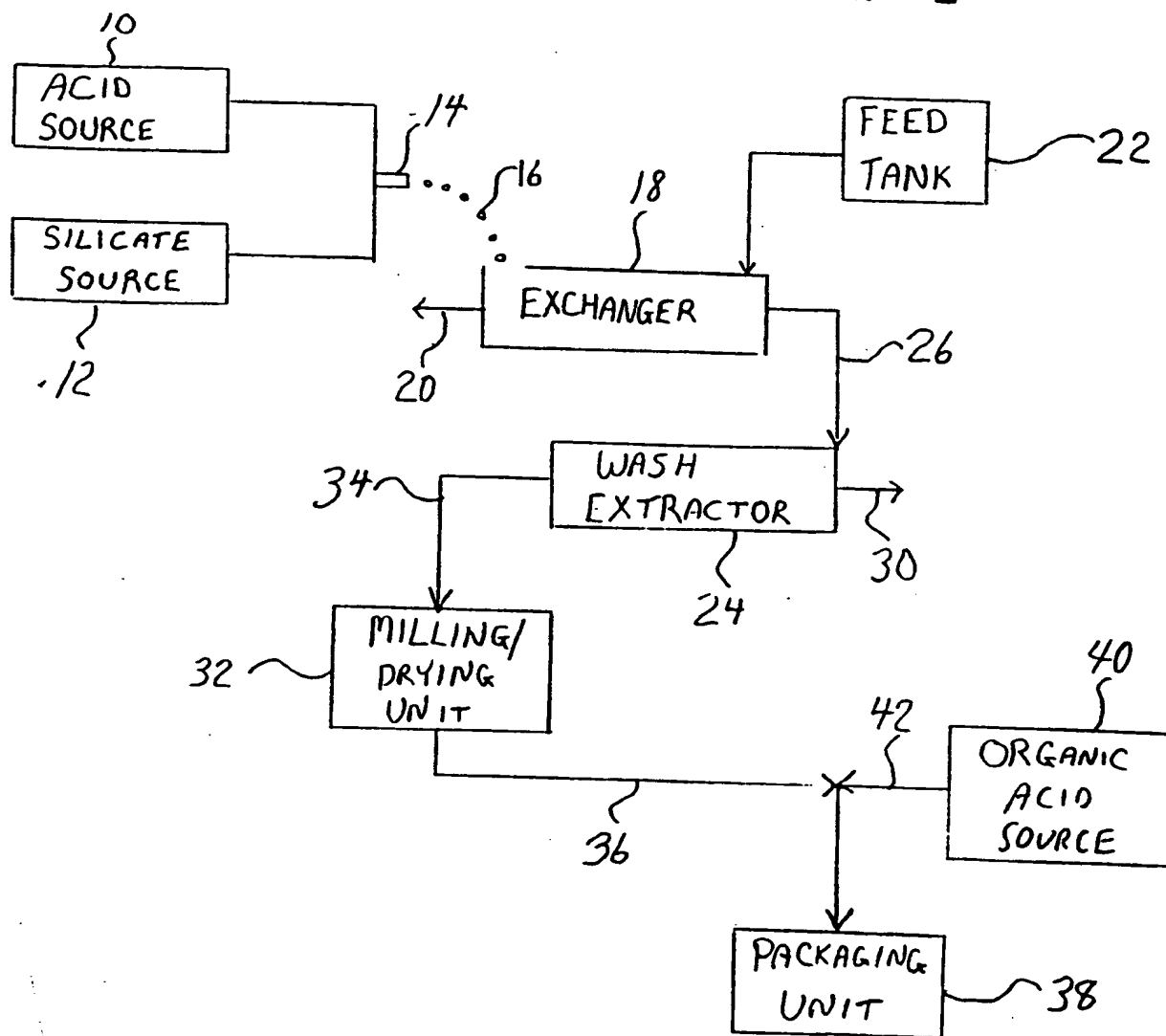
allowing said hydrosol to set to a hydrogel;
granulating said hydrogel into discrete hydrogel particles;
washing said discrete hydrogel particles with water;
drying and milling the reacted silica material; and
5 combining tannic acid powder with said dried silica material to form said
adsorbent.

10 25. A method in accordance with claim 24, wherein the combining step
comprises selecting the compositions and proportions of said silicate solution and said acid
solution such that 60% to 99% by weight of the sodium or potassium in the silicate solution
is neutralized and said method further comprises, prior to the washing step, contacting said
discrete hydrogel particles with a solution of a salt of a multivalent metal and maintaining
the pH of the mixture of the hydrogel and solution at a value between about 7 and 10.5, to
allow said metal to exchange with the sodium or potassium to form a metal-substituted,
silica hydrogel.

15 26. A method in accordance with claim 24, wherein the drying step
continues until said reacted silica material has a moisture content of between about 0.01%
and about 25%.

27. An adsorbent formed by the process of claim 24.

FIGURE 1



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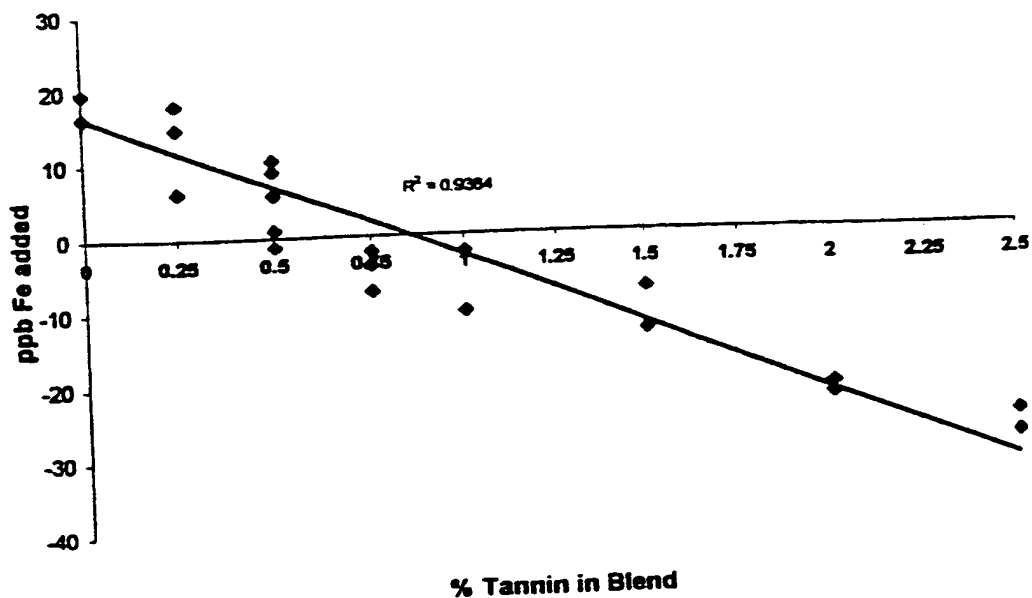


Figure 3

Fe Contributed to Beer at Various Contact Times
(Total Fe value - Fe of Untreated Sample)

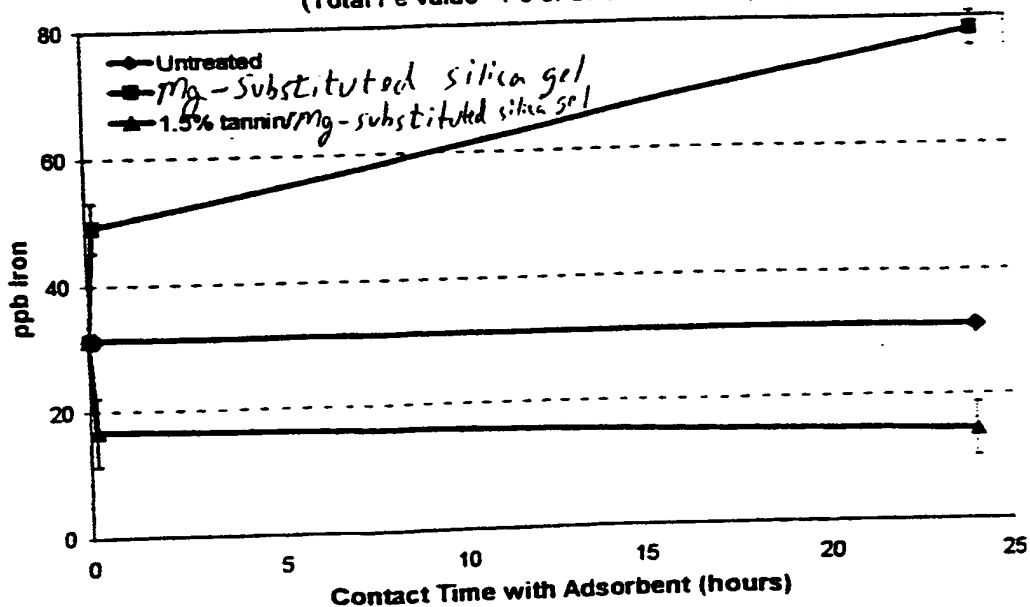
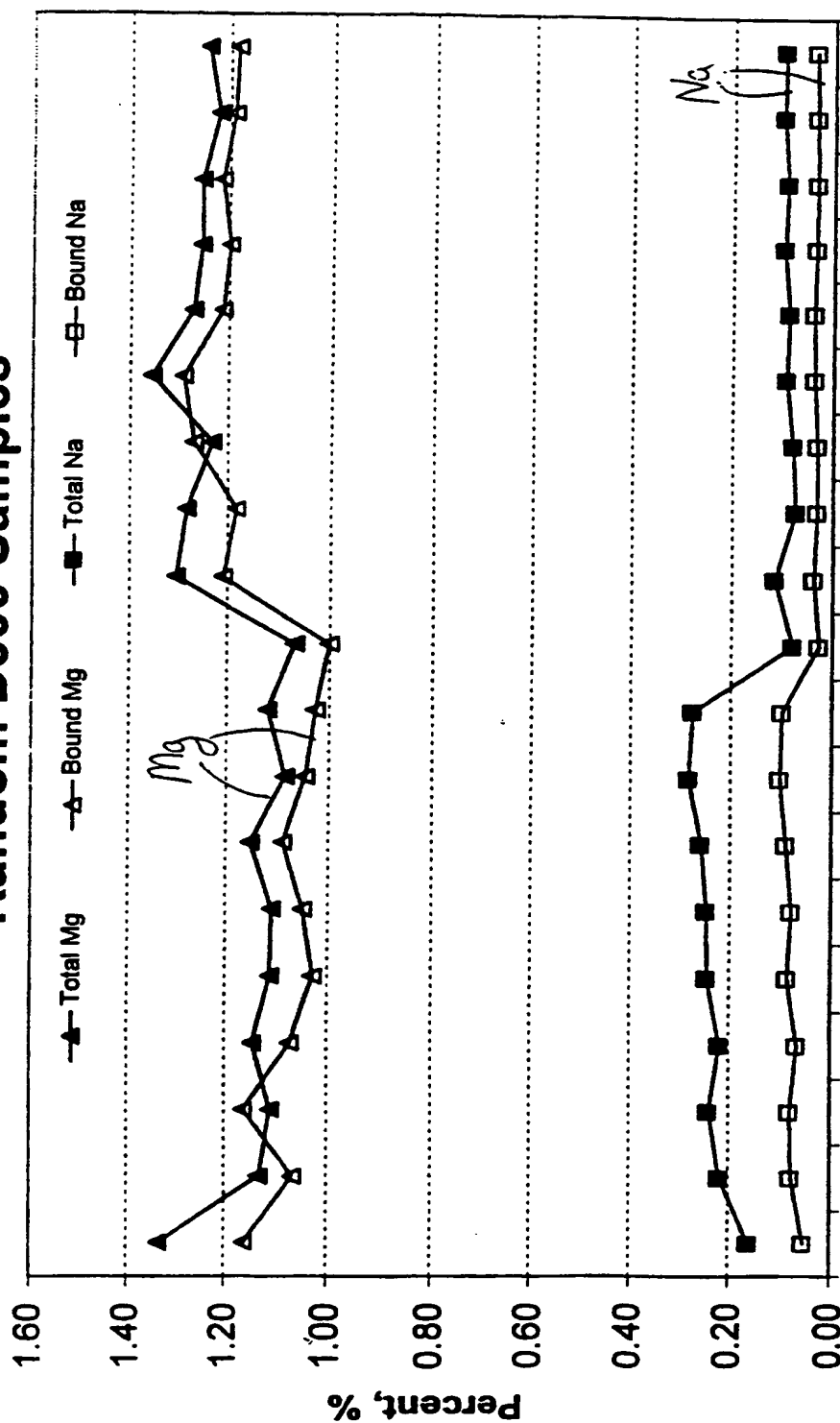


Figure 4

Bound and Total Sodium and Magnesium of Random D300 Samples



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(54) Title: PROCESS AND COMPOSITION FOR REDUCING CHILL HAZE IN BEVERAGES

(57) Abstract: A process and composition for removing certain undesirable components from beverages which tend to form a haze upon chilling utilizes an adsorbent including a silica component and a tannic acid component. The form of the silica component includes a silica gel and a metal-substituted silica gel, preferably a magnesium-substituted silica xerogel. The form of the tannic acid component includes tannic acid powder, in which case the adsorbent is simply a physical blend of tannic acid powder and the silica component. The form of the tannic acid component also includes a reaction product of tannic acid formed on the silica component during formation, such as by washing the silica hydrogel with a tannic acid solution. The adsorbent is particularly well-suited to reducing chill haze in beer. In addition to removing proteins which cause chill haze, the adsorbent of the present invention tends to remove some other components such as iron, without requiring the time-consuming process steps of allowing adsorbent to settle and decanting the beverage as is normally the case with tannin chillproofing and without requiring excessive energy to be applied during filtration.

INTERNATIONAL SEARCH REPORT

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B. FIELDS SEARCHED

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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, FSTA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 006 356 A (MUNSON JAMES R) 9 April 1991 (1991-04-09)	1,5-7, 11, 15-17, 20,23, 24,27 8,10
A	column 1, line 7 - line 15 column 2, line 22 - line 33 column 2, line 58 -column 3, line 21 ---	
X	EP 0 118 990 A (CORNING GLASS WORKS) 19 September 1984 (1984-09-19) page 1, line 4 - line 9; claims 1,3,4; example 1 page 2, line 12 - line 26 --- -/--	1,11,20, 23,24,27

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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